Relation of Land Use to Nitrogen Concentration in Ground Water in the Patuxent River Basin, Maryland

By E. Randolph McFarland

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	Ву	To obtain
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
acre	0.4047	hectare
square mile (mi ²)	2.590	square kilometer
gallon per minute per foot [(gal/min)/ft]	0.2070	liter per second per meter

Abbreviated water-quality units: Chemical concentrations are reported in milligrams per liter (mg/L). Milligrams per liter represents the mass of solute per unit volume (liter) of water.

Relation of Land Use to Nitrogen Concentration in Ground Water in The Patuxent River Basin, Maryland

By E. Randolph McFarland

Abstract

A decrease in nitrogen inputs could improve water quality in Chesapeake Bay. In order to provide information about nitrogen transport to the bay, the U.S. Geological Survey examined historical land use associated with nonpoint sources of nitrogen and nitrogen concentrations in ground water in the Patuxent River Basin, a major tributary to the bay in Maryland.

Most nitrogen in ground water in the Patuxent River Basin was present as nitrate. In the Piedmont Physiographic Province part of the basin, nitrate concentrations in ground water were higher in agricultural areas than in forested and urban areas. Nitrate concentrations were related to land use at well sites because wells vielded water that infiltrated within the same area where the wells are located. Agricultural activities possibly were a source for the transport of large amounts of nitrogen to ground water and probably also to base flow in nearby streams. The high nitrate concentrations were not attributed to sampling bias.

In the Coastal Plain Physiographic Province part of the basin, most nitrate concentrations were low and were unrelated to land use at the well site because the wells were screened in deep, regional aquifers. Ground water in a few shallow wells had high nitrate concentrations, possibly related to nearby agricultural and urban land use. Increased nitrate concentrations in shallow ground water could increase concentrations in stream base flow and eventually could increase concentrations in regional aquifers and ground water that discharges directly to Chesapeake Bay.

INTRODUCTION

The diminished natural and economic productivity of Chesapeake Bay has been attributed to degradation of water quality from numerous sources of contamination (Chesapeake Implementation Committee, 1988). Large

amounts of nitrogen in many parts of the bay result in eutrophic conditions that are deleterious to aquatic ecosystems. As a result, nitrogen is considered among the most important contaminants in the bay. A major goal of the Chesapeake Bay restoration effort is to decrease the amount of nitrogen that is transported to the bay by 40 percent by the year 2000 (Chesapeake Implementation Committee, 1988).

Excess nitrogen in Chesapeake Bay originates from nonpoint sources, such as farmland, lawns, septic systems, and atmospheric emissions, and from point sources, such as sewage and industrial discharges (Chesapeake Implementation Committee, 1988). Reducing the amount of nitrogen and other contaminants from nonpoint sources is more difficult than from point sources because the characteristics of nonpoint sources are more diverse and complex. Contaminant types, amounts, and transport processes from nonpoint sources to the bay are not well

Most research on Chesapeake Bay water quality has focused on the main stem of the bay or its tributary streams. However, ground water is recognized increasingly as an important transport medium for nitrogen and other contaminants to the bay (Chesapeake Bay Research Conference, 1990). Historically, research on ground water within the bay watershed has focused on the potential of aquifers as sources for water supplies. Less information exists on the interaction of ground water with surfacewater bodies that can transport contaminants to the bay.

The U.S. Geological Survey (USGS), in cooperation with the Maryland Department of the Environment, is studying the effects of different nonpoint sources of contaminants on water quality in the Patuxent River, Maryland, a major tributary to Chesapeake Bay, and on the water quality of the entire bay watershed (Summers, 1986). Components of these studies include the transport of nitrogen to ground-water and surface-water systems and the bay.

Purpose and Scope

This report describes the relation of different land uses associated with nonpoint sources of nitrogen to the concentration of nitrogen in ground water within the Patuxent River Basin in Maryland. Historical groundwater data from the USGS National Water Information System (NWIS) data base are presented. Concentrations of different nitrogen species in ground water are compared. Statistical relations between different land uses and concentrations of nitrate (a species of nitrogen) in ground water are examined. Gaps in existing data are identified, and implications of nitrogen transport in ground water that is discharged to streams and coastal areas are discussed.

Description of Study Area

The Patuxent River is 110 mi long and drains an area of about 930 mi² from central Maryland to the western shore of Chesapeake Bay (fig. 1). The climate throughout the basin is humid and temperate, with warm summers and mild winters. Annual precipitation is approximately 43 in. The basin contains two distinctly different physiographic provinces—the Piedmont Physiographic Province (Piedmont) and the Coastal Plain Physiographic Province (Coastal Plain). The Fall Line separates the Piedmont to the northwest from the Coastal Plain to the southeast.

The headwaters of the Patuxent River are in the Piedmont (fig. 1), which generally is characterized by rolling terrain. The Piedmont contains igneous and metamorphic rock of Late Proterozoic and early Paleozoic age, as well as basins of Mesozoic age that contain downfaulted sedimentary rock, igneous rock, and associated thermally metamorphosed rock. Bedrock is overlain by as much as 100 ft or more of regolith, which generally consists of a granular residual layer of saprolite (derived from weathering of underlying bedrock) and thin, discontinuous alluvial deposits (Heath, 1984).

The middle and lower parts of the Patuxent River Basin lie within the Coastal Plain (fig. 1), which is characterized by rolling terrain with deeply incised stream valleys in the northwestern part, and gently rolling-to-level terrain in the southeastern part. The Coastal Plain is underlain by a seaward-thickening wedge that contains southeastward-dipping strata of unconsolidated to partly consolidated sediment of Cretaceous, Tertiary, and Quaternary age (fig. 2) (Glaser, 1971). The strata

unconformably overlie Piedmont rock. The Fall Line is the westernmost extent of the sediment wedge and defines the boundary between the Coastal Plain and Piedmont (figs. 1 and 2). The thickness of the sediment wedge in Maryland ranges from 0 at the Fall Line to more than 8,000 ft along the Atlantic Coast (Cushing and others, 1973). Near the mouth of the Patuxent River, the thickness is about 3,000 ft (Overbeck, 1951).

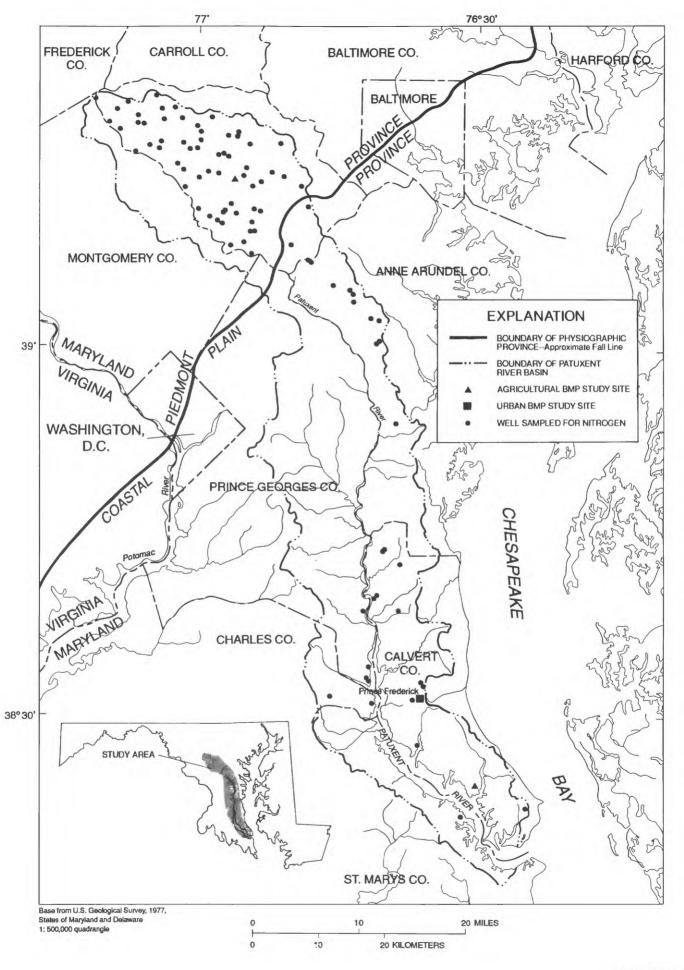
Ground-Water Movement

Ground water in the Piedmont is present in regolith in pores between sediment grains and in bedrock fractures. Because of limited availability, ground water in the Piedmont generally is used only for domestic and small public supplies. Some shallow bored wells draw water from regolith, but deeper drilled wells that draw water from the fractured bedrock system are more common.

Ground water in the Piedmont is recharged by precipitation that infiltrates the land surface and percolates through the unsaturated zone to the water table. From the water table, water flows downward because of gravity and laterally to streams. The flow generally does not cross topographic divides (fig. 2) (Richardson, 1980). Water is stored in regolith and is released slowly to bedrock fractures (Heath, 1984). Some fractures that are interconnected, transmit water to discharge zones. However, stream base flow is supplied largely by ground-water discharge from regolith (Nutter and Otten, 1969). Because of closely spaced stream networks, ground-water flow systems in the Piedmont are localized (LeGrand, 1967). Perennial stream basins define individual ground-water flow cells that generally are separate from adjacent cells (fig. 2) (Harned, 1989).

The sediment sequence in the Coastal Plain forms a geohydrologic framework of aquifers and confining units (fig. 2) (Meng and Harsh, 1988). Permeable formations from which substantial amounts of water are withdrawn are considered aquifers, and less permeable formations that partly restrict ground-water flow are confining units. Because of their relatively high yield and areal extent, Coastal Plain aquifers provide an important and extensively used ground-water supply (Heath, 1984).

Figure 1. Physiographic provinces, locations of wells sampled for nitrogen, and best-management practices (BMP) study sites in the Patuxent River Basin, Maryland.



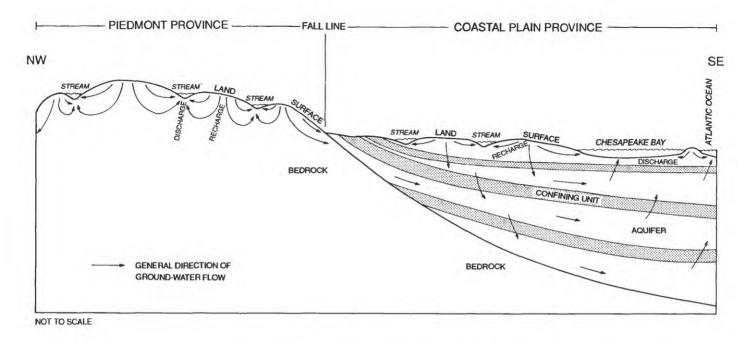


Figure 2. Conceptual hydrogeologic section showing general direction of ground-water movement in the Piedmont and Coastal Plain Physiographic Provinces of Maryland.

Unconfined ground water in the Coastal Plain is recharged by precipitation that infiltrates the land surface and percolates through the unsaturated zone to the water table. Most of the unconfined ground water flows short distances and discharges to nearby streams, but a small amount leaks downward to recharge the deeper aquifers (fig. 2). Flow through the confined aquifers is primarily lateral in the downdip direction to the southeast and toward major discharge areas near large rivers and coastal water (Harsh and Laczniak, 1990). Water is discharged from confined aquifers by upward leakage across intervening confining units to the discharge areas.

Land Use

Land use in the Patuxent River Basin historically has consisted of an approximately equal mix of forested and agricultural land (Maryland Office of Planning, written commun., 1988). Forested land generally is not associated with any major nonpoint sources of nitrogen and can be a sink for nitrogen associated with precipitation. Agricultural land can be a nonpoint source of nitrogen from fertilizer and manure applications to crops and other agricultural practices. Application of fertilizer and manure in agricultural areas has increased during the second half of the 20th century in concert with increased crop and livestock production.

The Patuxent River Basin has become increasingly urbanized during the second half of the 20th century. During 1973–90, the amount of urban land increased from 12 to 20 percent of the area of the basin (Maryland Office of Planning, written commun., 1988). Residential and commercial development, with a smaller amount of industrial development, has increased throughout the basin in response to increasing populations in the Baltimore, Maryland, and Washington, D.C. metropolitan areas. Forested and agricultural land have been converted to urban uses. Urban land can be a nonpoint source of nitrogen from private septic systems and fertilizer applications to lawns in residential and commercial areas.

Methods of Investigation

Historical ground-water data that were collected for previous studies by USGS personnel from within the Patuxent River Basin were retrieved from the USGS National Water Information System (NWIS) data base. The data are stored on a computer at the USGS office in Towson, Md. Data access and retrieval were accomplished using the NWIS Water-Quality (QWDATA) and Ground Water Site Inventory (GWSI) systems (Maddy and others, 1989).

Concentrations of nitrogen species in 106 groundwater samples collected throughout the Patuxent River Basin (hereafter referred to as "basinwide" data) were retrieved for this study. Only concentrations of total nitrite plus nitrate, nitrite, and ammonium in unfiltered groundwater samples were available for samples basinwide. Dissolved-oxygen concentrations also were retrieved for the basinwide samples as were characteristics of the wells from which the samples were collected, including well depth, specific capacity, water-level depth, casing depth, topographic setting, and aquifer lithology.

For comparison purposes, extensive ground-water data also were retrieved that were collected at two sites within the Patuxent River Basin (fig. 1) for an earlier study of the effects on ground water of agricultural bestmanagement practices (BMP's) (McFarland, in press), and at a third site for a separate study of the effects on ground water of urban BMP's (Wilde, 1989) (fig. 1). Data from these studies (hereafter referred to as "BMP" data) are documented in written communications and a referenced report, and include concentrations of dissolved nitrite plus nitrate, nitrite, ammonium, and organic nitrogen plus ammonium in filtered ground-water samples.

The Patuxent River Basin was delineated by using geographic data that characterize areas as having different types of forested, agricultural, or urban land uses. The data are based on 1:62,500-scale maps updated with high altitude aerial photography (Maryland Office of Planning, written commun., 1988). Data analysis was accomplished using the geographic information system (GIS) ARC/ INFO¹ (Environmental Systems Research Institute, 1987, 1989) on the computer system at the USGS office in Towson, Maryland.

Acknowledgments

The author wishes to thank Dr. Robert M. Summers of the Maryland Department of the Environment for assistance in the planning and direction of this study. Thanks also are extended to the many owners of wells who granted permission for the collection of water-quality and well-characteristic data.

NITROGEN CONCENTRATION IN GROUND WATER

Concentrations of nitrogen in 106 ground-water samples collected from wells throughout the Patuxent River Basin (fig. 1, table 1) were examined to determine the distribution of nitrogen among different nitrogen species. Concentrations of nitrogen species, including nitrate (NO_3^-) , nitrite (NO_2^-) , and ammonium (NH_4^+) , in the unfiltered basinwide ground-water samples were measured. Organic nitrogen also can be present in ground water but was not analyzed in the basinwide samples. Reporting limits generally were 0.1 mg/L for nitrate and 0.01 mg/L for ammonium and nitrite, although a few lower concentrations were reported for nitrate. All but one of the samples had nitrate concentrations that were less than the Federal drinking-water regulation of 10 mg/L (U.S. Environmental Protection Agency, 1990).

The largest concentrations of nitrogen in the basinwide samples were in the form of nitrate (fig. 3). Concentrations less than the reporting limit were plotted as equal to the reporting limit. Similarly, at the BMP study sites, the concentration of nitrate in filtered ground-water samples was higher than that of other forms of dissolved nitrogen, including organic nitrogen (Wilde, 1989; McFarland, in press). Nitrogen concentrations in the unfiltered basinwide ground-water samples were comparable to nitrogen concentrations in the filtered BMP groundwater samples because most of the nitrogen in ground water is usually dissolved.

Dissolved nitrogen can change from one form to another depending on the chemical environment (Klein and Bradford, 1979). Most of the transformation reactions are biologically mediated. Organic nitrogen from biological sources at the land surface reacts to form ammonium (NH₄⁺), which can be partially removed from solution by adsorption onto solid particles. If the concentration of dissolved oxygen is sufficiently high, ammonium that is not adsorbed is changed to nitrite (NO₂⁻):

$$2 NH_4^+ + 3 O_2 \rightarrow 2 NO_2^- + 4 H^+ + 2 H_2O.$$
 (1)

Nitrite is an unstable transition product and is quickly changed to nitrate (NO₃⁻):

$$2 \text{ NO}_{2}^{-} + \text{O}_{2} \rightarrow 2 \text{ NO}_{3}^{-}$$
 (2)

Thus, organic nitrogen at the land surface that was transported by percolation to ground water in the Patuxent River Basin was converted to nitrate.

¹The use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

[ft, feet below land surface; (gal/min)/ft, gallons per minute per foot; mg/L, milligrams per liter; <, less than; --, data unavailable or not used in study. Source: Land-use data from Maryland Office of Planning. Other data from U.S. Geological Survey data bases] Table 1. Characteristics of selected wells and concentrations of selected constituents in ground water in the Patuxent River Basin, Maryland

The captal cap	Moll minet	110/M	Water-	Total	9	, v	1	٣	Land use³	e	Sampling	Ø	Selected constituents (mg/L)	ituents (ng/L)
100 138 0.43 MS		well depth (ft)	depth (ft)	depth (ft)	specinic capacity [(gal/min)/ft]	Aquiler lithology ¹	setting ²	1	1985	1990	date (month- day-year)	Nitrate as N	Ammonium as N	Nitrite as N	Dissolved
150 150 138 0.43 MS						Piedı	nont Physiogra	phic Pro	vince						
600 450 161 .13 IMI flat FAU FU FU 66-26-89 <.10 005 <.01 225 35 61 .36 IMI slope A A A O5-22-90 3.5 .01 0.05 .01 .02 .01 .01 .01 .01 .01 .01 .01 .01 .01 .02 .01 .01 .01 .02	390734076475401	150	100	138	0.43	MS	flat	江	江	FO	12-14-88	<0.10	;	<0.01	3.7
1, 2, 2, 3, 5, 6, 1, 3, 6, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1,	390742076481401	009	450	161	.13	IMI	flat	FAU	FU	교	06-26-89	<.10	0.05	<.01	.05
1.240 80 29 .03 MS slope A U U 05-29-90 1.0 .01	390800076541601	225	35	19	.36	IMI	slope	Ą	∢	4	05-22-90	3.5	.03	.01	8.4
125 38 33 .12 IMI hillop F F F 12-14-88 1.7 01 300 40 53 .01 MS hillop A A A 07-03-89 130 .02 .01 300 MS hillop A A 07-03-99 1.1 .01 .01 165 45 68 .05 IMI hillop A A A 07-03-99 1.1 .01	390849076563201	240	80	59	.03	MS	slope	Ą	D	n	05-29-90	1.0	<.01	<.01	5.1
300 40 53 .01 MS hillup A A A O7-03-89 13.0 .02 <01 300 MS slope F F U 01-09-90 1.1 0.0 <01	390852076500701	125	38	33	.12	IMI	hilltop	Щ	щ	щ	12-14-88	1.7	1	.01	8.1
300 MS slope F F U 01-09-90 1.1 0.0 340 45 68 .05 IMI hilltop A A A 04-17-90 <.10	390908076553005	300	40	53	.01	MS	hilltop	Ą	Ą	Ą	07-03-89	13.0	.02	<.01	4.7
165 45 68 .05 IMI hilltop A V 11-08-89 .90 <.01 340 70 71 .01 IMI hilltop A A 04-17-90 <.01	390936076581702	300	1	;	;	MS	slope	江	Щ	D	01-09-90	1:1	.01	<.01	5.1
340 70 71 .01 IMI hilltop A A A O4-17-90 <.10 <.01 <.01 205 25 61 .06 IMI slope FU F F 06-19-89 <.10	391001076542401	165	45	89	.05	IMI	hilltop	Ą	D	D	11-08-89	96.	<.01	<.01	6.8
255 25 61 .06 IMI slope IU U 05-24-90 2.6 <.01 <.01 160 30 30 1.00 IMI slope FU F 66-19-89 <.10	391004076540301	340	70	71	.01	IMI	hilltop	Ą	4	4	04-17-90	<.10	<.01	<.01	5.6
160 30 30 1.00 IMI slope FU F F 06-19-89 <-10 <01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01 <-01	391042076572601	205	23	61	90:	IMI	slope	D	n	D	05-24-90	5.6	<.01	<.01	∞i
1 - - - IMI bottom A A A A 65-08-89 3.5 .02 <01 205 45 36 .06 MS hilltop F U 06-08-89 1.8 .02 .01 400 20 46 .02 IMI slope A A A A .02 .01 .01 .02 .03 .03 .02 .03<	391046076542601	160	30	30	1.00	IMI	slope	B	щ	щ	06-19-89	<.10	<.01	<.01	14.6
205 45 36 MS hilltop F U 06-06-89 4.1 .02 .01 10 10-25-89 4.1 .02 .01 .01 .01 .02 .03 .	391054076575801	1	;	;	ŀ	IMI	bottom	Ą	4	Ą	05-08-89	3.5	.02	<.01	7.2
1 205 45 36 0.06 MS hilltop F U 06-06-89 1.8 <.01 <.01 <	391054076575801	1	1	;	ł	IMI	bottom	Ą	Ą	٧	10-25-89	4.1	.02	.01	6.2
4 00 20 46 0.2 IMI slope A A Designation A A A Designation A A A A A A A A A A A C-17-90 7.5 < 0.1	391111076585101	205	45	36	90:	MS	hilltop	Щ	D	n	68-90-90	1.8	<.01	<.01	10.4
365 24 43 04 IMI slope A U 11-20-89 <.10 0.0 <td>391130076555901</td> <td>400</td> <td>8</td> <td>46</td> <td>.02</td> <td>IMI</td> <td>slope</td> <td>4</td> <td>Ą</td> <td>4</td> <td>05-17-90</td> <td>7.5</td> <td><.01</td> <td><.01</td> <td>6.2</td>	391130076555901	400	8	46	.02	IMI	slope	4	Ą	4	05-17-90	7.5	<.01	<.01	6.2
1 120 15 62 .19 IMI bottom A U 04-05-90 2.5 <.01 <.01 1 100 20 19 .29 IMI slope A A A A 11-29-89 2.0 <.01	391135076571701	305	24	43	\$	IMI	slope	Ą	Ą	D	11-20-89	<.10	.02	.02	ιi
100 20 19 .29 IMI slope A A 11-29-89 2.0 <.01 <.01 500 30 28 .07 IMI bottom F F F 11-01-89 <.10	391138076532401	120	15	62	.19	IMI	bottom	Ą	D	n	04-05-90	2.5	<.01	<.01	5.6
500 30 28 .07 IMI bottom F F I-01-89 <.10 <.01 <.01 1 280 40 20 .08 MS bottom FU U 01-18-89 <.10	391146076570701	100	8	19	.29	IMI	slope	Ą	4	٧	11-29-89	2.0	<.01	<.01	9.9
280 40 20 .08 MS bottom FU U 01-18-89 <.10 <.01 1 150 35 27 .15 IMI hilltop F U U 04-10-90 .80 <.01	391149076540101	200	30	78	.07	IMI	bottom	Щ	Щ	ഥ	11-01-89	<.10	<.01	<.01	1.7
150 35 27 .15 IMI hilltop F U U O4-10-90 .80 .01 .01 .01 .01 .01 .02 .02 .02 .02 .02 .02 .03	391149077000301	280	4	70	80:	MS	pottom	H	딢	D	01-18-89	<.10	1	<.01	1.1
150 20 51 .12 IMI hilltop U U F 10-25-89 5.3 .02 .02 .03 .04 .	391216076480101	150	35	27	.15	IMI	hilltop	江	D	D	04-10-90	.80	<.01	<.01	1.8
. 140 27 48 .30 MS hilltop A F 04-24-90 2.8 <.01	391220076563301	150	20	51	.12	IMI	hilltop	D	D	讧	10-25-89	5.3	.02	<.01	6.2
. 120 50 78 .14 IMI slope U A U 06-06-89 2.2 <.01 .160 40 77 .17 IMI flat A U 06-19-89 1.1 <.01	391338077013001	140	27	48	.30	MS	hilltop	∢	щ	;	04-24-90	2.8	<.01	<.01	7.5
160 40 77 .17 IMI flat A U 06-19-89 1.1 <.01	391346076541501	120	20	78	.14	IMI	slope	Ω	¥	n	68-90-90	2.2	<.01	<.01	9.4
	391353076490301	160	4	11	.17	IMI	flat	4	D	!	06-19-89	1.1	<.01	<.01	7.8

footnote at end of table

Table 1. Characteristics of selected wells and concentrations of selected constituents in ground water in the Patuxent River Basin, Maryland—Continued

p lealing de	0		2000	Choolfio	Agrifar	Tonographio	i			e dob	ı	(1 S)		î b
	_	depth (ft)	depth (ft)	capacity [(gal/min)/ft]	Iithology ¹	setting ²	1973	1985	1990	day-year)	Nitrate as N	Ammonium as N	Nitrite as N	Dissolved oxygen
			į		Piedmont P	Piedmont Physiographic Province—Continued	rovince	Conti	nued					
391409076532201	88	20	56	0.17	IMI	hilltop	Ą	n	Ą	06-26-89	1.3	0.01	<0.01	7.4
391426076595701	165	65	53	60:	MS	slope	Ą	¥	Ą	05-24-90	1.5	<.01	.02	9.4
391438076505801	160	9	65	80:	IMI	hilltop	ഥ	Ħ	교	05-03-90	1.4	<.01	<.01	9.1
391441076551201	400	33	33	4.	IMI	slope	Ą	٧	;	05-08-90	7.3	<.01	<.01	5.9
391448076575501	245	38	45	.27	MS	hilltop	Ą	Ą	Ą	05-22-90	5.0	<.01	<.01	7.4
391456076585801	200	59	62	.20	MS	hilltop	∢	Ą	Ω	06-27-89	69:	.02	.01	11.6
391503076521301	160	63	\$	1	IMI	hilltop	ഥ	n	ഥ	06-14-89	3.7	.01	<.01	6.7
391506077013401	140	9	78	;	WS	slope	¥	Ą	}	05-03-90	1.6	<.01	<.01	10.1
391525076544901	125	30	8	.32	IMI	slope	ഥ	Þ	n	06-05-89	3.2	.02	.01	9.5
391534077021701	;	;	1	1	MS	pottom	ഥ	ഥ	ഥ	05-08-89	3.6	.01	<.01	10.3
391534077021701	;	;	;	ŀ	MS	bottom	IТ	ப	ц	10-25-89	6.2	.02	<.01	0.6
391543076564901	180	20	30	90.	IMI	bottom	Ľ	n	D	11-20-89	2.5	.02	.02	9.9
391620076575801	128	2	99	.20	MS	hilltop	∢	D	n	03-28-89	8.9	4	<.01	7.8
391626076572301	58	4	52	33	MS	hilltop	n	n	Ω	02-27-90	7.3	<.01	<.01	9.4
391627077064401	203	126	112	.15	MS	hilltop	4	4	;	05-08-90	5.6	<.01	<.01	8.2
391645077041601	225	\$	19	.19	MS	slope	ц	n	n	11-29-89	<.10	<.01	<.01	10.1
391647077005801	103	23	31	!	MS	flat	٧	Ą	Ω	01-09-90	6.9	<.01	<.01	9.0
391652077001301	105	4	45	.46	MS	flat	$\mathbf{A}\mathbf{U}$	ΑU	n	03-20-89	5.8	.07	<.01	5.9
391702077051401	100	30	21	.11	MS	hilltop	Ą	٧	Ą	05-01-89	4.9	.01	<.01	5.7
391714076543801	453	45	62	.10	MS	slope	吐	Ą	D	05-31-90	40	<.01	<.01	0.8
391718077014301	145	45	62	.10	MS	slope	Þ	Ą	IL	12-09-88	3.8	1	<.01	8.4
391720077040101	100	23	9	.29	MS	slope	AU	n	n	11-08-89	3.9	<.01	<.01	8.2
391724076512001	140	55	47	.12	IMI	slope	Ω	Ω	n	05-15-89	9.6	<.01	.01	5.7
391726076565802	82	35	46	.40	MS	slope	Ą	\mathbf{AU}	Ω	02-27-90	9.4	.01	<.01	7.7
391733076595301	80	30	21	.20	MS	slope	FA	FA	n	03-28-89	8.0	.02	<.01	8.0
391753076555801	300	9	47	.02	MS	bottom	ഥ	Ω	n	03-27-89	.10	<.01	<.01	7
391813076554701	145	9	36	.13	MS	slope	ഥ	FU	n	01-24-90	2.2	.03	<.01	2.3
391813076555601	410	25	20	.01	MS	hilltop	ц	口	}	02-06-90	1.2	<.01	<.01	8.3
391815076595401	165	45	43	9:00	MS	hilltop	Ą	AU	Ľ	02-06-90	5.9	<.01	<.01	9.2
		•	•	(00		5		

footnote at end of table

Table 1. Characteristics of selected wells and concentrations of selected constituents in ground water in the Patuxent River Basin, Maryland—Continued [ft, feet below land surface; (gal/min)/ft, gallons per minute per foot; mg/L, milligrams per liter; <, less than; --, data unavailable or not used in study. Source: Land-use data from Maryland Office of Planning. Other data from U.S. Geological Survey data bases]

\$ \bar{\bar{\bar{\bar{\bar{\bar{\bar{	(f) (T) (T) (T) (T) (T) (T) (T) (T) (T) (T	n _	capacity [(gal/min)/ft]	lithology¹ Piedmont P	setting ²	1973	1985	1990	(month-	Nitrate	Ammonium	Nitrite	Dissolved
	. 60 . 00 . 00 . 00 . 00 . 00 . 00 . 00	20 20 49 48 33 33 37	- 29 - 29 - 20 - 20	Piedmont P					day-year)	as N	as N	as N	61
	. 00 00 00 00 00 00 00 00 00 00 00 00 00	1 2 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	- 29 - 20 - 20	MS	Piedmont Physiographic Province—Continued	rovince	-Conti	pənu					
	000 000 000 000 000 000 000 000 000 00	20 49 48 33 34 26 37	29 <.01 <.01 01 1.11 25 25		bottom	Ą	FA	ഥ	04-17-90	2.2	<0.01	<0.01	1
	50 50 50 50 50 54 54 50	49 48 38 37 26	6.01 6.01 10. 11.11 25.	MS	slope	4	FA	¥	04-11-90	6.1	<.01	<.01	9.4
	50 50 50 45 45	48 48 38 37 26	501 .01 .11 .25	MS	slope	江	ഥ	ഥ	05-01-89	1.3	.01	<.01	2.1
	50 50 54 54 54	48 33 37 26	.01 1.11 25	MS	slope	江	ഥ	ഥ	11-01-89	1.5	.01	<.01	9.3
391851077063301 240	50 29 45	38 37 26	.18 1.11 25	MS	slope	FA	FA	щ	05-01-90	1.2	<.01	<.01	0.9
391910077034501 200	65 2	37	1.11	MS	slope	¥	n	n	05-31-90	8.0	<.01	<.01	8.2
	45	26	.25	MS	slope	Ą	Ą	Ą	06-14-89	3.9	.01	<.01	8.1
	4D	•	ć	MS	hilltop	Ą	Ą	1	03-27-89	2.3	<.01	<.01	7.1
391929077062901 100	7	18	.53	MS	hilltop	Ą	A Π	Ω	04-10-89	1.5	<.01	<.01	7.3
391956077084501 300	55	19	.05	MS	hilltop	щ	Ą	;	04-26-90	4.9	<.01	<.01	10.9
392003077040501 200	45	19	9.	MS	slope	Ą	Ą	1	05-15-90	4.8	.02	<.01	7.8
	34	20	.15	MS	hilltop	Ą	Ą	;	05-22-89	2.5	.05	<.01	8.6
	52	54	.33	MS	slope	¥	¥	D	04-18-89	3.6	<.01	<.01	7.5
392043077105901 200	10	37	.02	MS	pottom	¥	щ	;	04-10-89	3.6	<.01	<.01	3.6
392057077043301 140	30	30	.18	MS	slope	Æ	D	n	02-09-89	2.3	.01	<.01	2.1
				Coasta	Coastal Plain Physiceraphic Province	Janhic F	Province	•					
					Road Target	· alle		,					
٠,	ţ	;	!	1	;	;	1	;	08-02-80	.11	;	}	:
	1	1	;	1	;	щ	Þ	n	08-02-80	.02	1	1	;
382732076355801 405	;	;	1	1	;	ц	щ	ц	08-80-80	.01	1	1	1
383051076404101 448	;	;	:	;	;	¥	¥	Ω	03-10-81	<u>\$</u>	;	;	}
383114076365001 315	1	1	1	1	1	щ	ц	U	08-80-80	60.	1	;	1
383120076451401 709	1	;	;	!	;	ц	щ	ц	01-30-75	.15	!	}	;
383239076354201 570	:	;	;	1	;	ц	FO	田	07-25-79	.02	;	:	1
383248076405303 1,070	ł	;	;	1	:	¥	Ą	¥	03-26-74	<.10	;	;	1
383248076405303 1,070	;	;	;	1	;	Ą	Ą	¥	08-31-84	<.10	1	;	1
383258076412101 1,080	1	;	;	;	;	ഥ	ഥ	ഥ	10-17-90	<.10	.17	<.01	}

Table 1. Characteristics of selected wells and concentrations of selected constituents in ground water in the Patuxent River Basin, Maryland—Continued

	Well	Water-	Total	o iii	A silifo	- decree	٣	Land use ³	6 0.	Sampling	Ö	Selected constituents (mg/L)	ituents (ng/L)
Well number	well depth (ft)	depth (ft)	depth (ft)	Specific capacity [(gal/min)/ft]	Aquirer lithology ¹	setting ²	1973	1985	1990	date (month- day-year)	Nitrate as N	Ammonium as N	Nitrite as N	Dissolved oxygen
					Zoastal Plain	Coastal Plain Physiographic Province—Continued	Provinc	- Coi	ıtinued					
383259076412701	1,060	i	1	1	ł	1	Щ	щ	Щ	11-16-90	<.10	0.23	<0.01	:
383348076411301	870	1	;	1	!	;	ц	Ц	Ц	01-24-75	.03	1	ł	;
383348076411302	654	i	;	1	1	1	江	Щ	ш	01-14-75	.03	1	;	1
383348076411303	376	!	ŀ	;	1	ı	Ц	ц	Ц	12-20-74	.01	1	;	;
383832076414701	1	1	1	1	1	}	∢	∢	ď	02-05-75	.01	ł	1	;
383837076381001	415	1	i	ł	ŀ	1	江	FA	FA	08-28-80	.01	ł	}	ł
383848076495801	422	}	;	;	t	1	1	;	;	05-15-78	.02	1	;	;
383931076405301	130	1	;	;	t	!	Ą	¥	V	08-28-80	.03	;	ł	;
383950076402801	285	1	ť	;	ł	1	FA	Ą	D	08-28-80	.28	;	;	1
384222076380101	342	1	;	;	t	1	FA	FU	FG.	08-28-80	80.	1	1	;
384333076394701	320	!	;	ł	ŧ	ı	;	ı	;	08-03-79	90.	;	}	;
384333076394702	170	1	;	•	;	1	;	1	;	06-27-80	<.10	ł	1	1
384715076522001	350	1	;	ŀ	1	ł	;	1	;	62-80-90	<.10	:	}	!
385406076383901	157	1	;	ł	!	1	∢	K	;	08-15-79	.02	ł	}	ł
390047076404901	1,180	1	;	ł	l	1	щ	ц	щ	07-12-74	.01	1	;	;
390100076403201	4,590	;	ŀ	1	ł	1	Ą	D	D	07-08-73	.005	1	500.	;
390103076402601	673	;	:	i	1	1	¥	Ą	Ą	07-19-79	<.10	:	;	!
390103076402602	486	;	;	ł	I	1	Ą	Ą	4	07-24-79	<.10	;	1	1
390103076402603	147	;	;	1	ŧ	1	Ą	Ą	¥	07-26-79	.02	1	;	;
390152076492601	468	:	i	1	ŧ	1	;	1	ł	08-50-90	90:	1	1	:
390247076403501	127	1	ł	;	1	ł	ΑU	ΑU	D	09-17-75	7.0	1	1	;
390254076413001	975	;	:	;	ŀ	ı	ц	D	Щ	10-28-76	<.10	1	ł	1
390419076431901	743	;	1	;	l	1	щ	щ	Щ	02-21-85	<.10	:	;	1
390457076432501	685	i	1	1	ł	;	Ą	щ	n	10-12-84	<.10	1	;	;
390512076434501	643	:	;	1	l	1	Ą	FU	D	10-18-84	<.10	1	;	1
390538076453002	479	1	1	ł	ŧ	1	щ	щ	Щ	82-20-90	<.10	;	1	;
								!						

¹Aquifer lithology: IMI, igneous and meta-igneous rocks; MS, meta-sedimentary rocks.

²Topographic setting as identified onsite or from topographic maps following Maddy and others, 1989.

³Land use: A, agricultural; F, forested; U, urban.

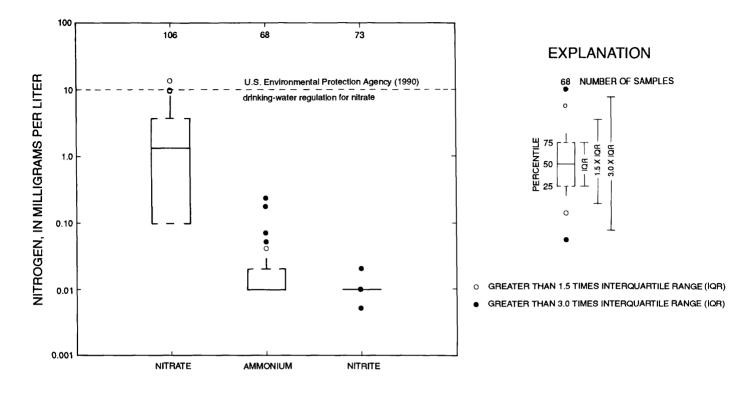


Figure 3. Concentrations of nitrogen species in ground water from the Patuxent River Basin, Maryland.

Nitrate can remain chemically stable in ground water under aerobic conditions but, under anaerobic conditions, it can undergo denitrification to form nitrogen gas (N₂):

$$4 \text{ NO}_3^- + 5 \text{ HCHO} \rightarrow 2 \text{ N}_2 + 5 \text{ CO}_2 + 4 \text{ OH}^- + 3 \text{ H}_2\text{O}.$$
 (3) (carbohydrate)

Nitrate also can be reduced to ammonium (NH₄⁺) in environments similar to those in which denitrification occurs, but relations between the two processes are not well known (Korom, 1992). Once N₂ is formed, however, it resists further reaction because of the strong triple bond between nitrogen atoms, and can be removed from ground water by diffusion. Ammonium, on the other hand, can remain dissolved in ground water and, if transported into an aerobic environment, can be oxidized back into nitrate.

Low dissolved-oxygen concentrations in ground water favor denitrification. However, low nitrate concentrations in the basinwide ground-water samples generally did not correspond to low dissolved-oxygen concentrations, indicating that the low nitrate concentrations were not due to denitrification. Spearman's rank correlation (Iman and Conover, 1983) for 70 samples with both nitrate and dissolved-oxygen concentration data yielded a

rho value of 0.10, which was less than the critical value of 0.15 at the 95-percent confidence level, and indicated no relation.

The extent of denitrification in ground water in the Patuxent River Basin is uncertain. Ground-water chemistry could have been too variable for denitrification to be apparent from the available data. For example, if denitrified ground water became re-oxygenated, then the low nitrate concentration would no longer correspond to a low dissolved-oxygen concentration. Denitrification could be evident in ground water with low concentrations of nitrate if high concentrations of N₂ were present. However, the basinwide ground-water samples were not analyzed for N₂, and therefore, the extent of denitrification cannot be assessed. Denitrification was indicated at the agricultural BMP study sites by low nitrate and dissolved-oxygen concentrations and other evidence in some parts of the aquifers, but N₂ concentrations were close to or only slightly greater than that in equilibrium with the atmosphere (McFarland, in press). The N2 could have diffused out of the aquifers (Korom, 1992), but the extent of basinwide N₂ diffusion is unknown.

RELATION OF LAND USE TO NITROGEN CONCENTRATION

Different nitrogen sources at the land surface can affect nitrogen concentrations in ground water by contributing different quantities of nitrogen transported to the aquifers during recharge. For the basinwide ground-water samples that were not affected by denitrification or ammonification, differences in concentrations of nitrate (the predominant form of nitrogen) probably resulted from differences in the amount of nitrogen transported to the aquifers.

Effects of Flow Paths and Traveltimes

Nitrate concentrations in basinwide ground-water samples were examined along with well depths to determine if nitrate concentrations in different hydrogeologic settings could be related to land-use activities and (or) other sources of nitrogen at the land surface. The basinwide samples were separated into 70 samples from wells located in the Piedmont and 36 samples from wells located in the Coastal Plain. Not all samples with nitrateconcentration data also had well-depth data (table 1). For comparison, nitrate concentrations in the BMP groundwater samples were represented separately by median values, for each well at the two agricultural study sites (McFarland, in press), one of which was located in the Piedmont and the other in the Coastal Plain, and for each well at the urban BMP study site (Wilde, 1989), which was located in the Coastal Plain (fig. 1). The BMP data were grouped separately from the basinwide data so as to not overrepresent conditions at the BMP study-site locations in the basinwide analysis.

Most of the basinwide wells located in the Piedmont were shallower than the basinwide wells located in the Coastal Plain, and had higher nitrate concentrations and a larger range of concentrations (fig. 4). A few of the Piedmont wells were as deep as most of the Coastal Plain wells and had similarly low nitrate concentrations.

Ground-water flow systems in the Piedmont are localized and correspond approximately to surface-drainage basins (fig. 2). Deep, areally extensive regional aquifers generally do not exist as in the Coastal Plain. The wateryielding properties of rock in the Piedmont decrease with depth, and consequently, most active wells draw water from within 300 ft or less of the land surface. Ground water is recharged within close proximity to the wells, and the water quality of these samples probably represents

recent land-use activities at the well sites. Several decades or more could be required for ground water to flow through the deepest parts of the flow systems, and consequently, the quality of deep ground water probably represents land uses from less-recent activities.

Most of the basinwide samples from the Piedmont contained water that infiltrated the land surface within the past several decades. During this period, large amounts of nitrogen from nonpoint sources have become widespread. including increased fertilizer and manure applications in agricultural areas and septic systems in residential areas. Ground-water flow systems throughout the Piedmont were not characterized in sufficient detail in this study to determine accurate traveltimes from recharge areas to specific wells. However, traveltimes were estimated at the agricultural BMP study site in the Piedmont (McFarland, in press), and ranged from 2 years or less for shallow ground water in regolith to several decades for deep ground water in bedrock. The agricultural BMP study site was located on a large research farm operated by the University of Maryland. Nitrate concentrations were related to well depth and were highest at shallow depths as a result of relatively recent agricultural practices. High nitrate concentrations in shallow wells elsewhere in the Piedmont probably resulted from recent agricultural practices or other land-use activities in the nearby vicinity of the wells.

Ground water in the Piedmont is discharged in the same surface-drainage basin where it is recharged, and stream base flow is supplied largely by discharge of shallow ground water from regolith. Consequently, the water quality of stream base flow represents relatively recent land-use activities in close proximity to the stream. Land uses that result in high nitrate concentrations in ground water in the Piedmont could ultimately result in high nitrogen species concentrations in the base flow of nearby streams within a period of several years.

Basinwide ground-water samples were collected in the Coastal Plain at only about half as many locations as in the Piedmont, resulting in a less-dense spatial distribution (fig. 1). In addition, most of the basinwide wells in the Coastal Plain were deeper than in the Piedmont (fig. 4) and were sampled for studies of water-supply aquifers that were confined and were recharged at locations several miles or more away from the wells (fig. 2).

Lower nitrate concentrations were found in water from most of the basinwide wells in the Coastal Plain than in water from wells in the Piedmont. The water quality of ground-water samples from the Coastal Plain probably was unrelated to land-use activities at the well sites.

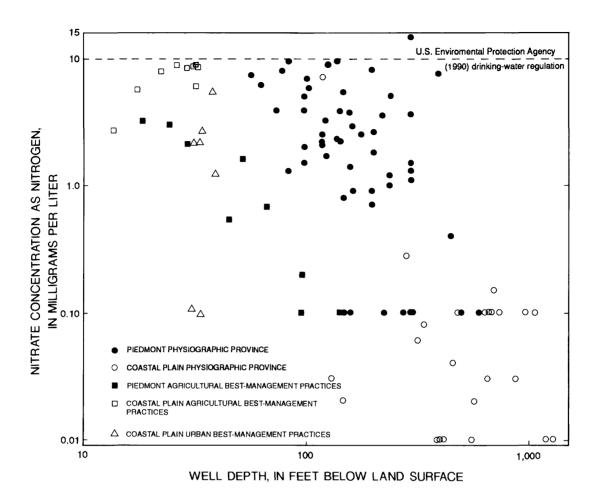


Figure 4. Relation of nitrate concentrations and well depths in the Patuxent River Basin, Maryland.

Ground water could take several decades or more to flow to the wells from distant recharge areas or leak through confining units. The water quality of the samples probably represents less-recent land-use activities in the Coastal Plain than in the Piedmont.

Most of the basinwide ground-water samples from the Coastal Plain had relatively low nitrate concentrations because the water sampled from the deep regional aquifers infiltrated the land surface before large quantities of nitrogen from nonpoint sources were applied extensively. The ground-water-flow system in the Coastal Plain was not characterized in sufficient detail in this study to determine accurate traveltimes from recharge areas to specific wells. However, some of the deep Coastal Plain aquifers extend for tens of miles from recharge areas to the well locations. Water from many of the wells probably infiltrated the land surface prior to the 1950's, before large

fertilizer and manure applications in agricultural areas and before septic systems in residential areas became widespread.

Within the Coastal Plain, wells at the agricultural and urban BMP study sites and one of the basinwide wells, were shallower and had generally higher nitrate concentrations than the rest of the basinwide wells (fig. 4). The agricultural BMP study site was located within a 500-acre area used historically for production of soybeans and corn (McFarland, in press). The urban BMP study site was located within residential and commercial areas in the town of Prince Frederick (Wilde, 1989). The shallow basinwide well was also in an urban area, near areas that were agricultural as recently as 1985. Although the data were limited, relatively high nitrate concentrations in these shallow wells in the Coastal Plain probably resulted from fertilizer applications in the vicinity of the wells. Similar increases in nitrate concentration in shallow

ground water were found to be widespread in other parts of the Coastal Plain in Maryland and were attributed largely to agricultural fertilizer applications (Hamilton and Shedlock, 1992).

Shallow ground water in the Coastal Plain is discharged to nearby streams. Land uses that result in high nitrate concentrations in shallow ground water probably will result in high nitrate concentrations in stream base flow as described for the Piedmont. However, for the Coastal Plain, shallow ground water also provides recharge to deep, areally extensive confined aquifers (fig. 2). Over several decades, land-use activities in regional recharge areas that increase nitrate concentration in shallow ground water could result in increased nitrate concentrations in the regional aquifers and, over longer periods, in increased nitrate concentrations in ground water that is discharged directly from the confined system to Chesapeake Bay and other coastal areas.

Stratification of Ground-Water Data

In order to determine the relation of different land uses to nitrate concentrations in ground water, the basinwide wells were classified as to location in different types of land use (table 1) using a geographic information system (GIS). Detailed data on land use in the Patuxent River Basin during 1973, 1985, and 1990 were used to delineate areas within the basin into three land-use types characterized as forested, agricultural, or urban (Maryland Office of Planning, written commun., 1988). Specifically, the three land-use types were-

- (1) Forested, including forest cover and wetlands;
- (2) agricultural, including cropland, pasture, animalproduction areas, and other agricultural areas; and
- (3) urban, including low-density residential and open urban areas, medium- and high-density residential and institutional areas, commercial and industrial areas, mineral-extraction areas, and barren areas.

Basinwide wells initially were grouped as being located in the Piedmont or the Coastal Plain, and were separated further into groups located within each of the three land-use types. Incomplete well-location and (or) land-use information resulted in some wells without landuse classifications (table 1). A few wells were located near boundaries between two different land-use areas and, because of accuracy limitations of the GIS, were classified as being in both land uses. Wells grouped in urban areas were located predominantly in residential areas, which included housing subdivisions on previously

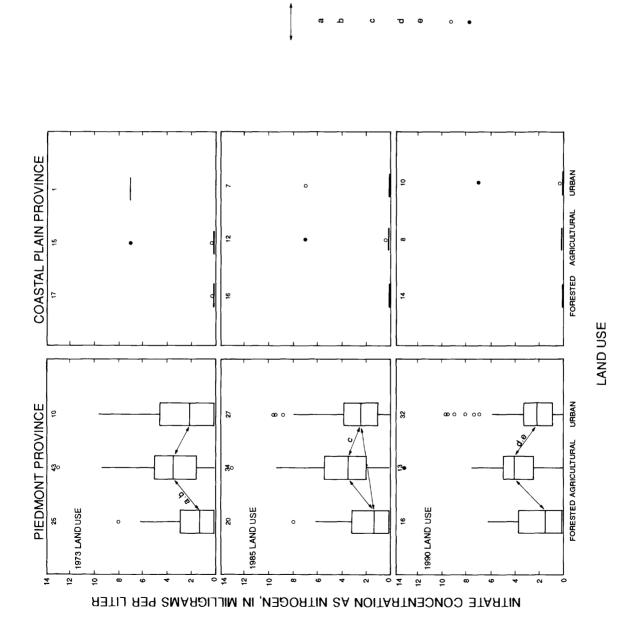
agricultural or forested land and small municipalities. Few wells were located in commercial or industrial areas because these activities typically are supplied with public water; therefore, nitrate concentrations in ground water resulting from these activities probably were not well represented.

Because ground-water flow rates differ, ground-water quality can be related to solute sources from different times in the past. In order to see if ground-water nitrate concentrations were more closely related to land use from one time rather than other times, the basinwide wells were grouped three ways on the basis of 1973, 1985, 1990 landuse data. Because the basin became more urbanized over time, the number of wells increased in urban areas during 1973-90 and decreased in forested and agricultural areas.

Differences in Nitrate Concentration Resulting from Land-Use Activities

Nitrate concentrations of the basinwide ground-water samples are summarized for each of the land-use types (fig. 5). Differences in nitrate concentration between wells located in different land uses in the Piedmont are probably the result of nitrogen introduced to ground water from different land-use activities. Differences between nitrate concentrations in wells located in different land uses in the Coastal Plain were minimal (fig. 5) and were not related clearly to land use where the wells are located.

A series of Wilcoxin-Mann-Whitney rank-sum tests (Iman and Conover, 1983) was performed to determine if differences in the nitrate concentrations of the basinwide ground-water samples from the Piedmont were statistically significant among the land-use types. The tests were performed on nitrate-concentration data between pairs of land-use types. The procedure tested the assumed hypothesis that the nitrate concentrations from two land-use types came from the same population of all nitrate concentrations; the alternative hypothesis was that the concentrations from the land-use types came from different populations. Because the procedure was performed on the ranks of the data, it did not depend on the data being normally distributed and could be used with censored data that had multiple reporting limits (Helsel and Hirsch, 1992). The tests produced probability (p) values that indicated the degree of confidence with which the alternative hypothesis, that nitrate concentrations from land-use types were different, could be accepted. Differences were



SIGNIFICANTLY DIFFERENT NITRATE CONCENTRATIONS

RANK-SUM TEST)

30 NUMBER OF SAMPLES

3.0 IQR ADI 2.1 ROI

PERCENTILE % 22

52

EXPLANATION

1973 FORESTED WATER LEVELS DEEPER THAN 1973 AGRICULTURAL WELL WATER LEVELS

1973 FORESTED WELLS DEEPER THAN 1973 AGRICULTURAL WELLS

GREATER THAN 1.5 TIMES INTERCUARTILE RANGE (IQR) GREATER THAN 3.0 TIMES INTERQUARTILE RANGE (IQR)

1990 AGRICULTURAL WELL CASING DEEPER THAN 1990 JRBAN WELL CASING 1985 AGRICULTURAL WELL DISSOLVED-OXYGEN CONCENTRATIONS GREATER THAN 1985 URBAN WELL DISSOLVED-OXYGEN CONCENTRATIONS

1990 AGRICULTURAL WELL SPECIFIC CAPACITY LESS THAN 1990 URBAN WELL SPECIFIC CAPACITY

Figure 5. Nitrate concentrations in ground water in areas of different physiography and land use in the Patuxent River Basin, Maryland.

considered significant for tests that produced p values of 0.10 or less, which represented confidence levels of 90 percent or greater.

For land-use types based on 1973, 1985, and 1990 data, nitrate concentrations were highest in agricultural areas and differed significantly from forested and urban areas (table 2, fig. 5). By contrast, nitrate concentrations differed significantly between forested and urban areas only for land-use types that were based on 1985 data. No significant difference was found between forested and urban areas for land-use types that were based on 1973 and 1990 data.

Within the Piedmont in the Patuxent River Basin. nitrate concentrations in ground water were generally higher in agricultural areas than in forested and urban areas, possibly because agricultural land-use activities release larger amounts of nitrogen to ground water than activities in forested and urban areas. If so, then agricultural land use probably also contributes larger amounts of nitrogen to the base flow of nearby streams.

For the land-use types based on 1973, 1985, and 1990 data, some nitrate concentrations could be more closely related to the land use of each year than other nitrate concentrations, depending on the ages of the ground-water samples. For example, nitrate concentrations in young ground-water samples result from more recent land use than nitrate concentrations in older ground-water samples: the nitrate concentration in ground water that infiltrated in 1990 is unrelated to land use in 1973. If the ages of the ground-water samples were known, only samples with ages that correspond to the year of each land-use type could be included, and other samples could be excluded. However, the specific ages of individual ground-water samples are unknown and all ground-water samples were included in the land-use types for all 3 years. The groundwater samples range in age and can be as old as several decades in the Piedmont, and older than several decades in the Coastal Plain. As a result, the nitrate concentrations for each land-use type could be partly homogenized, and some differences among the land-use types could exist that are not made apparent by comparing nitrate concentrations.

Potential Differences in Nitrate Concentration Resulting from Sampling Bias

Several factors that could be related to ground-water nitrate concentrations, and could result in sampling bias in the nitrate-concentration data were examined. Sampling

bias could produce statistically significant differences in nitrate concentrations among the land-use types that are unrelated to land use. Some factors other than land use that could affect nitrate concentrations are—

- (1) Denitrification, indicated for this study by dissolvedoxygen concentration;
- (2) depth of the flow system, indicated by well depth;
- (3) thickness of the unsaturated zone, indicated by static water-level depth;
- (4) thickness of regolith, indicated by well-casing depth;
- (5) position within the flow system, indicated by topographic setting; and
- (6) hydraulic properties of the aquifer, indicated by specific capacity and aquifer lithology.

With the exception of denitrification, the factors are related to the age of the sampled ground water and the relative position within the ground-water flow system from which the sample was collected. For example, wells in agricultural areas could be significantly shallower than wells in forested areas. Because shallow wells generally contain young water that is affected by recent large nitrogen sources at the land surface, the nitrate concentrations could be higher in the shallow wells than in the deep wells. In this case, the wells in agricultural areas could have higher nitrate concentrations than the wells in forested areas as a result of being shallower, and not necessarily because agricultural land-use activities result in transport of larger amounts of nitrogen to ground water. Similarly, young ground water and high nitrate concentrations could result from thin unsaturated zones and (or) regolith, locations near surface-discharge zones, such as at the bottoms of slopes, and (or) high hydraulic conductivity of aquifer materials.

Differences among the land-use types in continuous factors, including well depth, water-level depth, dissolved-oxygen concentration, casing depth, and specific capacity, were determined by performing Wilcoxin-Mann-Whitney rank-sum tests between pairs of land-use types (table 2). Not all wells with nitrate-concentration data also had data on all of the factors (table 1). For landuse types that had significantly different nitrate concentrations, five instances (footnoted a-e in table 2 and fig. 5) also differed significantly (at the 90-percent confidence level) with respect to one of the above factors that could account for the differences in nitrate concentrations. In these cases, factors other than land use could have produced the statistically significant differences in nitrate concentrations. In three additional instances (1973 agricultural and urban wells, 1985 forested and urban wells, and 1990 agricultural and forested wells), differences

Table 2. Wilcoxin-Mann-Whitney p values for rank-sum tests on ground-water data from wells located in the Patuxent River Basin and Piedmont Physiographic Province in Maryland

	19	73 land use		19	85 land use		19	90 land use	•
Type of data	Agricul- tural and forested	Agricul- tural and urban	Forested and urban	Agricul- tural and forested	Agricul- tural and urban	Forested and urban	Agricul- tural and forested	Agricul- tural and urban	Forested and urban
Nitrate concentration	0.0001	0.03	0.21	0.0008	0.08	0.05	0.0008	0.001	0.20
Finished well depth	a.01	.15	.002	.14	.12	.01	.30	.18	.02
Water-level depth	b.03	.30	.18	.32	.43	.40	.15	.42	.16
Dissolved-oxygen concentration	.14	.05	.26	.45	°.03	.14	.06	.30	.11
Well-casing depth	.22	.21	.10	.39	.26	.14	.11	d.09	.39
Specific capacity	.14	.16	.03	.34	.19	.15	.36	e.07	.26

^a1973 forested wells deeper than 1973 agricultural wells.

between the factors were statistically significant but were not consistent with the differences in nitrate concentrations. Dissolved-oxygen concentrations were lower and well depths were greater for samples with high nitrate concentrations than for samples with low nitrate concentrations. Therefore, the nitrate-concentration differences in these three instances could not be accounted for by the differences in the factors.

For instances a through e, the possibility that factors other than land use are affecting nitrate concentration was tested further. For a difference in one of the factors between two land-use types to result in sampling bias in the nitrate concentrations, a relation would have to exist between nitrate concentration and the factor in question. To determine if any such relations existed, Spearman's rho rank correlation coefficients were calculated from the data on nitrate concentrations and each of the factors for each of the instances in which the factors differed between land-use types (fig. 6). Spearman's rho measures the strength of increasing or decreasing relations between nitrate concentrations and each of the factors (Iman and Conover, 1983). Its value can range from 1 for a perfect increasing relation to -1 for a perfect decreasing relation, with 0 for no relation. Because the procedure was used on the ranks of the data, the relation did not have to be linear,

and the data did not have to be normally distributed and could be censored with multiple reporting limits (Helsel and Hirsch, 1992).

In order to determine the significance of relations between nitrate concentrations and each of the factors, values for Spearman's rho were compared to tabulated critical values (Iman and Conover, 1983) for 90-percent and higher confidence levels. In most of the instances, no relation between nitrate concentrations and the factor was significant. In three instances, relations had marginal significance. The relation of nitrate concentrations to waterlevel depth in 1973 agricultural wells (instance b) was significant at the 90-percent confidence level but not at the 95-percent confidence level. Relations of nitrate concentrations to dissolved-oxygen concentrations in 1985 agricultural and urban wells (instance c), and to specific capacity in 1990 urban wells (instance e), were significant at the 90-percent and 95-percent confidence levels but not at the 99-percent confidence level.

Differences among the land-use types in the categorical factors of topographic setting and aquifer lithology were determined by computing test statistics from contingency tables (Iman and Conover, 1983) (tables 3 and 4). The contingency tables describe the number of samples from different topographic settings and aquifer lithologies

^b1973 forested water levels deeper than 1973 agricultural water levels.

c1985 agricultural dissolved-oxygen concentrations higher than 1985 urban dissolved-oxygen concentrations.

d1990 agricultural well casings deeper than 1990 urban well casings.

e1990 agricultural specific capacities higher than 1990 urban specific capacities.

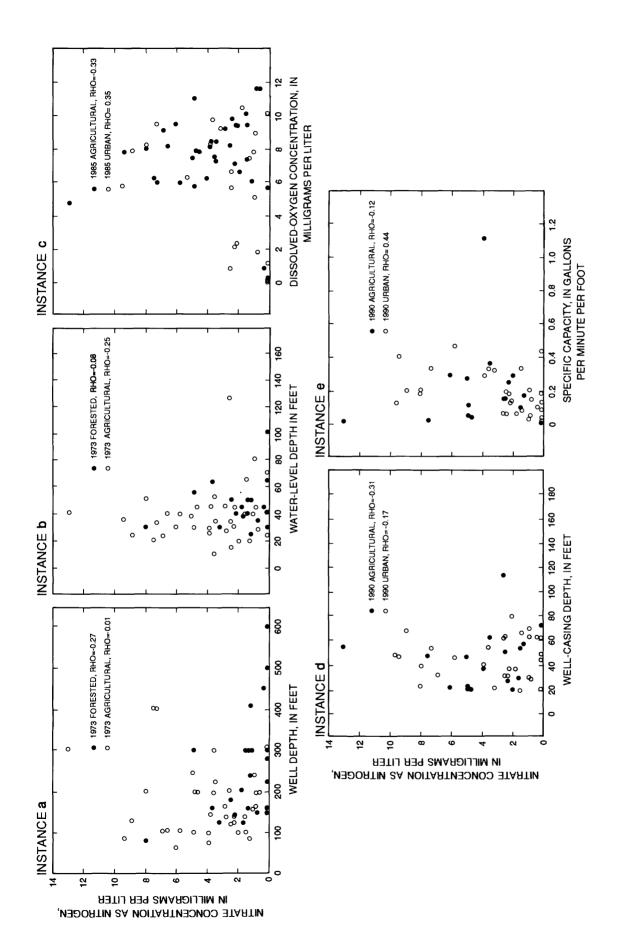


Figure 6. Concentrations of nitrate in ground water and factors affecting the concentration, Patuxent River Basin, Maryland.

for each land-use type. Topographic setting was categorized by descriptive terms to indicate the relative positions of the wells in the landscape, as identified onsite or from topographic maps. Aquifer lithology was generalized into two categories on the basis of 15 geologic formations in which the wells were completed, as identified onsite or from geologic maps. The lithologies have different porosity values that can affect the hydraulic properties of the aquifer materials. Igneous and metaigneous lithologies include six formations, and represent highly crystallized materials with low porosity. Metasedimentary lithologies include nine formations and represent partly crystallized materials that could have larger porosity.

The contingency tables tested the assumed hypotheses that the topographic settings and aquifer lithologies were the same among the land-use types, against the alternative hypotheses that the settings and lithologies differed among the land-use types. The test statistics had associated p values (similar to those for the Wilcoxin-Mann-Whitney rank-sum test) that indicated the degree of confidence with which the alternative hypothesis was accepted—that topographic setting or aquifer lithology differed among the land-use types.

In most cases, topographic setting and aquifer lithology did not differ among land-use groups. At the 90-percent confidence level, none of the groups differed significantly with respect to topographic setting (table 3), and aquifer lithology differed significantly only among groups based on 1973 land use and not among groups based on 1985 and 1990 land use (table 4).

Limitations of Available Data

The difference in nitrate concentrations among landuse types was shown to be caused primarily by land use and not generally by other factors that create sampling bias. However, these conclusions are limited by the quality of the data. Data used in this study were collected primarily from readily accessible water-supply wells and not from a network of observation wells designed to accurately characterize ground-water conditions in the basin. The specific ages of individual ground-water samples are unknown and could not be directly related to the land use of different years. Nitrate concentrations in ground water in commercial and industrial areas probably were poorly represented. Additional factors that affect nitrate concentrations other than those examined in this study also could exist. Although sampling bias was

Table 3. Contingency table for sample locations in various topographic settings and land-use types, Patuxent River Basin, Maryland [p, probability value]

	Num	ber of san	ple location	s
Land use	Hilltop	Slope	Bottom	Flat
1973	land use, test	statistic =	4.00, p = 0.6	8
Forested	7	11	6	2
Agricultural	16	20	6	4
Urban	2	7	1	2
1985	land use, test	statistic =	6.59, p = 0.3	6
Forested	4	9	6	2
Agricultural	14	19	3	2
Urban	10	10	5	3
1990	land use, test	statistic =	6.34, p = 0.3	9
Forested	5	6	4	2
Agricultural	10	8	2	0
Urban	9	17	5	4

Table 4. Contingency table for sample locations in various aquifer lithologies and land-use types, Patuxent River Basin, Maryland

[p, probability value]

	Number	of sample locations			
Land use	Igneous and meta-igneous lithology	Meta-sedimentary lithology			
197	73 land use, test stati	stic = 6.81 , $p = 0.03$			
Forested	10	12			
Agricultural	12	32			
Urban	8	4			
198	85 land use, test stati	stic = 4.35 , $p = 0.11$			
Forested	6	11			
Agricultural	8	27			
Urban	13 14				
199	90 land use, test stati	stic = 3.61 , $p = 0.16$			
Forested	8	5			
Agricultural	5	13			
Urban	13	20			

generally not proved to exist, it can never be proved not to exist. Relations among nitrate concentrations and any of the factors could exist that were not apparent from the limited available data.

SUMMARY AND CONCLUSIONS

Historical ground-water data were analyzed statistically to determine the relation of land use to nitrogen concentrations in ground water in the Patuxent River Basin in Maryland. Water samples collected from wells throughout the Patuxent River Basin initially were separated into those from the Piedmont and those from the Coastal Plain. Using land-use data for 1973, 1985, and 1990, the samples were grouped further into those collected from forested, agricultural, and urban land-use types for each of the three years.

Nitrogen in ground water in the basin was present primarily in the form of nitrate. Most of the ground-water samples from the Piedmont had higher nitrate concentrations than those from the Coastal Plain. Samples from the Piedmont contained water that infiltrated the land surface within the same surface-drainage areas in which the wells were located and within the past several decades, during which the quantity of nitrogen available from nonpoint sources increased. Therefore, nitrate concentrations in the Piedmont probably represented land use at the well sites, and differences in nitrate concentration among different land-use types probably resulted from the availability and transport of nitrogen from land-use activities to ground water. Ground water in the Piedmont generally is discharged close to where it is recharged. Therefore, land uses that resulted in high nitrate concentrations in ground water probably also resulted in high nitrate concentrations in the base flow of nearby streams.

Wilcoxin-Mann-Whitney rank-sum tests indicated that nitrate concentrations in ground water within the Piedmont in the Patuxent River Basin were higher in agricultural areas than in forested and urban (predominantly residential) areas. Agricultural land-use activities apparently introduced larger amounts of nitrogen to ground water than activities in forested and urban areas. In some cases, wells in agricultural areas differed from wells in forested and urban areas with respect to factors other than land use that could affect nitrate concentration. However, tests for correlation generally did not indicate relations among nitrate concentrations and these factors. Therefore,

differences in nitrate concentrations among areas of different land use were attributable primarily to land use. Factors other than those examined in this study could exist that could affect nitrate concentrations. Relations among nitrate concentrations and any of the examined factors could also exist that were not apparent from the available data.

Ground-water samples collected from the Coastal Plain in the Patuxent River Basin were fewer, were generally from deeper wells, and had lower nitrate concentrations than samples from the Piedmont. Most of the ground-water samples from the Coastal Plain were collected for studies of confined water-supply aquifers that were recharged several decades or more ago at locations several miles or more away from the wells and before the quantity of nitrogen available from nonpoint sources increased. Consequently, nitrate concentrations were low. Differences in nitrate concentration among different landuse types in the Coastal Plain were minimal and apparently were not related to land use at the well sites.

A small number of ground-water samples collected from the Coastal Plain were from shallow wells and had high nitrate concentrations that probably resulted from agricultural and urban land-use activities at the well sites. Land uses that resulted in high nitrate concentrations in shallow ground water in the Coastal Plain probably also resulted in high nitrate concentrations in stream base flow, as in the Piedmont. Additionally in the Coastal Plain, high nitrate concentrations in shallow ground water eventually could lead to increased nitrate concentrations in regional confined aquifers and ground water that is discharged from the confined system to Chesapeake Bay and other coastal areas.

Ground-water studies in the Coastal Plain historically have focused on regional aquifers for water-supply development and have not addressed possible effects on ground-water quality from contamination of the shallower unconfined aquifer. Additional data are needed on shallow ground water to determine the effects of different land-use activities on nitrogen concentrations in ground water in the Coastal Plain.

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